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Metallurgical Factors Influencing Direct Laser Deposition of Metallic Powders for Unitized Structures

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Final Performance Report

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Abstract
The aim of this project is to investigate the possibility of making use of direct laser deposition techniques for the production of unitized structures. Specifically, the research is directed at determining the metallurgical factors that influence the process for this application. By so doing, it is intended to develop technologies which permit exploitation of the advantages of this processing technique. This research that has been performed during the scope of this program has been considerable. Specifically, the research has been focused on process optimization and baseline property determination, graded compositions and the development of an associated combinatorial approach, the use of elemental blends, and the use of forging preforms. These represent the four primary research areas in this program, as described in the narrative below.

Motivation
There is currently considerable effort underway in industry aimed at employing unitized structures in airframes. The motivation for this effort is involved in effecting reduced manufacturing costs and reductions in weight. For example, a wing of an F-16 jet consists of over three hundred sub-components and over 20,000 fasteners, requiring considerable hours of labor which gives rise to the high cost of manufacture. Additionally, each hole drilled for a fastener is a potential fatigue crack initiation site, and so a significant reduction in such holes would have a markedly beneficial influence. Unitized structures would be produced with very much reduced numbers of manufacturing steps with an attendant decrease in costs. Clearly, marked advantages would be realized if it were possible to produce a wing consisting of one or two parts.

In this project, the possibilities of making use of direct laser deposition for fabricating unitized structures is being investigated. There are a number of advantages to making use of direct laser deposition for the production of such structures, the most obvious being that the processing technique is ideally suited for this purpose. Because of the efficient coupling between radiation from a Nd-YAG laser and Ti alloys, these alloys have been chosen as the subject of study in this project. There are a number of potential metallurgical advantages which need to be studied and exploited. These include the use of graded compositions and elemental blends, and the exploitation of the rapid rates of heat extraction associated with the process. Additionally, the use of laser deposits as forging performs is expected to reduce the costs of manufacture of a number of aerospace components, and so it is important that this possibility be investigated. The activities of this research project are centered on these various metallurgical and processing factors.

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14. ABSTRACT

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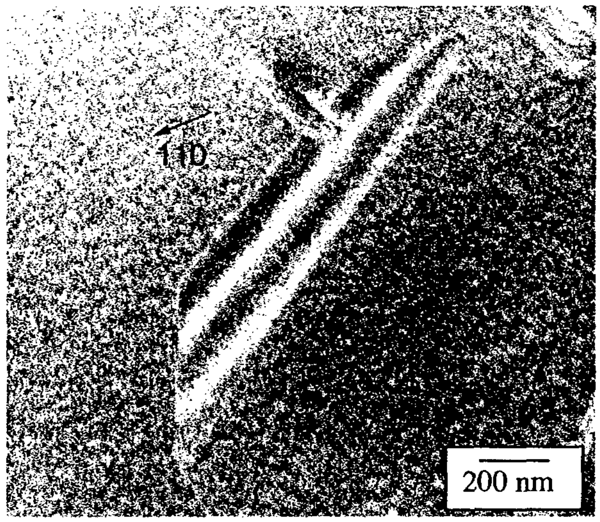


Fig. 1: Brightfield TEM micrograph of as-deposited β-21S.

Research Activities

There are four main research activities, involving process optimization and baseline properties, graded compositions, elemental blends, and the use of laser deposits as forging performs. The motivation and research activities for each of these areas during this reporting period are described below.

1. Process Optimization and Baseline Properties

Motivation: The purpose of this task is to determine the properties of different Ti alloys processed using direct laser deposition, having first optimized the processing parameters for the OSU LENS™ system. The primary laser processing parameters which may be optimized are laser power, travel speed, hatch width, layer spacing, and powder flow rate.

Originally, optimization was taken to mean the production of material with a minimum in % porosity which is also free of cracks. During the first reporting period, research was performed with the alloys Ti-6-4 and b-21S, the choices being simply determined by the acquisition of the appropriate prealloyed powders. The optimization procedure involves determining the processing windows that give rise to the minimum in the degree of porosity, yield homogeneous material, and have optimal mechanical properties. An example of the results of the optimization are presented for the case of β-21S. Fig. 1 shows a TEM micrograph of the material produced (for the first time) using LENS™. Interestingly, the material contains faults as well as a mottled contrast which when taken together with the diffuse scattering in the accompanying diffraction pattern reveals the presence of the ω-phase. Table 1 shows the influence of power density and powder flow rate on the residual porosity, and a reasonably minimum value of < 1% is achieved.

Material	*Power Density* kJ/cm^3	*Powder Flow* rpm	*Porosity* %	*Quality*
β-21S	**68**	**2.75**	**5.4 ± 0.9**	
β-21S	**72**	**2.75**	**3.1 ± 1.0**	
β-21S	**82**	**2.75**	**2.6 ± 0.8**	
β-21S	**78**	**2.25**	**3.8 ± 1.1**	**Ok**
β-21S	**78**	**2.00**	**0.9 ± 0.1**	**Best**
β-21S	**78**	**1.75**	**1.5 ± 0.3**	**Bad**

Based on discussions with experts in

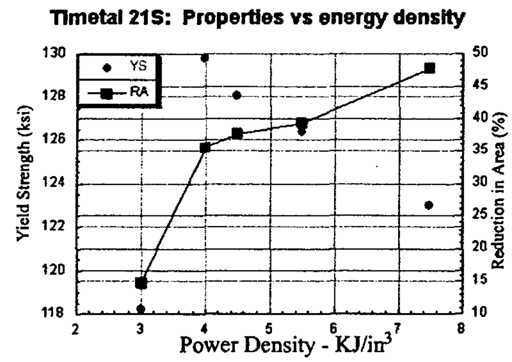


Fig. 2: Mechanical properties vs. laser processing parameters for β-21S.

the field, a slightly different analysis was used during the second phase of the program. This analysis limited the variables to power density (laser power, travel speed, hatch width, and layer spacing). Using such an approach, β-21S powder was deposited into cylindrical tensile bars using various power densities. These were machined, tested, and the results are shown in Fig. 2. As can be see, there is a critical energy density, after which, enough power has been input, and the mechanical tests yield mechanical properties that meet or exceed those of conventionally processed material. The mechanical property that is used to distinguish the critical energy density is ductility (% elongation or % reduction in area (RA)).

Considerable energy input is required to achieve such mechanical properties on the LENS™ system at OSU. Therefore, near the end of the program, an investigation into the purchase of a hot isostatic press (HIP) was initiated. The HIP ensures that acceptable mechanical properties are met at increased processing speeds. The designed HIP can operate at 1500°C and 30 ksi.

2. Graded Alloy Compositions

Motivation: A potentially major benefit is afforded by the application of direct laser deposition to unitized structures which involves the production of components with graded compositions. Thus, since the powders are deposited sequentially it is, in principle, possible to vary spatially the composition of the depositing powders. For example, it would be possible to locate an α/β alloy with a relatively high β-transus temperature (e.g., Ti-6-4: Tβ≈985°C) in a region where damage tolerance was required and then vary the composition such that another α/β alloy with a lower β-transus temperature (e.g., TIMETAL 555: Tβ≈865°C) would be located in a region requiring high strength. Heat-treatment, coupled with mechanical deformation, at a temperature of 900°C would cause the Ti-6-4 to consist of damage tolerant colony or basketweave microstructure whereas the TIMETAL 555 would have a microstructure consisting of equiaxed α-Ti and transformed β-Ti, imparting high ductility and strength.

The original research in graded compositions involved the study of some graded materials (γ-TiAl 48-2-2/Ti-6-2-4-2) supplied by Optomec while the OSU machine was being upgraded, and subsequently on compositions graded between CP-Ti/Ti-6-4. The choice of these latter materials for initiation of the research is based on their relative simplicity compared with the alloy combinations discussed in the proposal. Thus, the aim is to understand the parameters which influence the processing of useful graded materials and then to apply this understanding to the grading of more

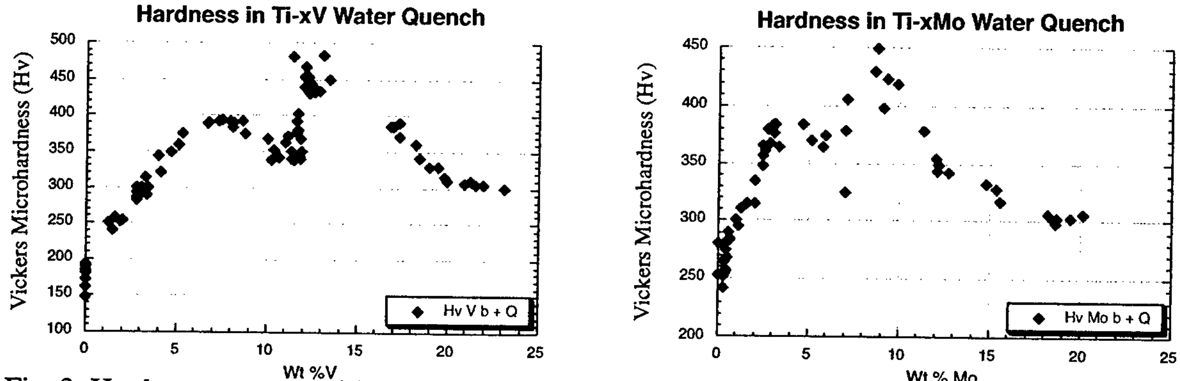


Fig. 3: Hardness vs composition in water quenched samples for (a) Ti-xV and (b) Ti-xMo complex alloys, as in the proposal (e.g., Ti-6-4/Ti-555, and Ti-6-4/β-21S).

The work performed in the second stage of the project involved elemental blended binary gradients. The motivation of this work was to develop an understanding of microstructure-property relationships. Specifically, as one grades from an α/β alloy to a β alloy, it is possible to pass through a region of limited ductility. Therefore, to successfully incorporate material models in the development of unitized structures, it would be important to understand the subtle microstructural changes that significantly impact the mechanical properties given small changes in composition. Thus, a rapid *combinatorial* approach to composition-microstructure-property relationships is required. For this work, various systems were studied in depth. These include Ti-xV, Ti-xMo, and Ti-6Al-xV. For the case of the first two, within a length of 2.5 cm, samples were graded from pure Titanium to Titanium + 25 wt% of Vanadium or Molybdenum. The samples were sliced so that each slice contained the whole gradient. Subsequently, they were β-solutionized, and cooled at different rates. The hardness variation vs. composition was measured for approximately 70 indents per sample. Some of these results are shown in Fig. 3. As can be seen for the water-quenched sample, there is a peak in the microhardness about halfway down the sample. During the remaining portions of this work, this peak is attributed to the precipitation of the athermal ω phase. Similar peaks in the air-cooled sample and furnace-cooled samples were attributed to the formation of secondary α. Such secondary α is shown in Fig. 4. While athermal ω is known to be an embrittling phase, the secondary α is known to strengthen the material. Therefore, material models

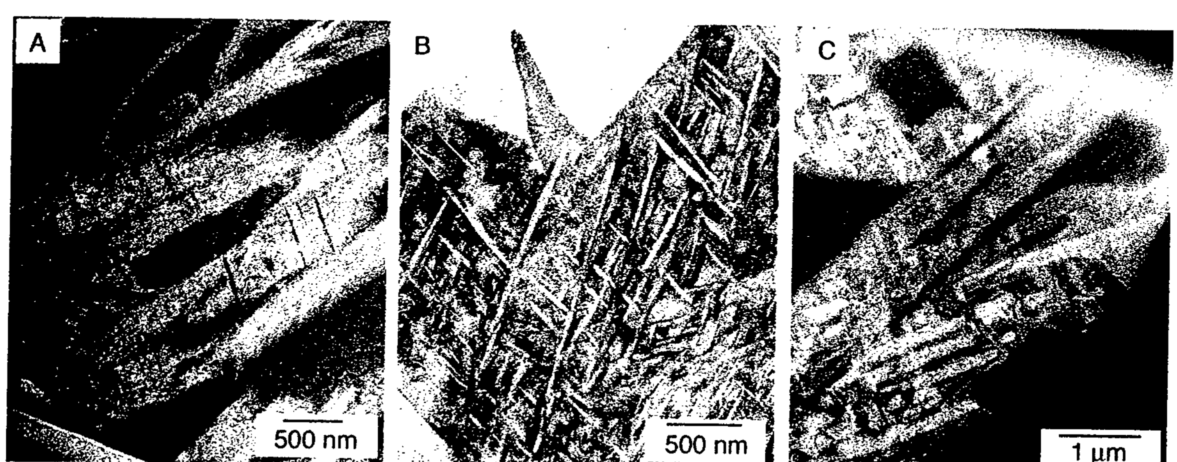


Fig. 4: Secondary α in furnace-cooled Ti-xMo

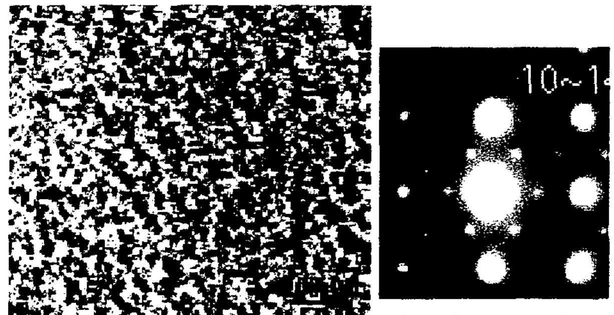


Fig. 5. TEM micrograph and representative diffraction pattern of a dispersion of particles of TiB in Ti produced in-situ by LENS™.

need to include the precipitation of such phases in order to further develop unitized structures.

3. Elemental Blends

Motivation: In the main, direct laser deposition has made use of pre-alloyed powders. When these powders are fabricated from high performance alloys, for example, Ti alloys for aerospace applications, they are rather expensive. High costs influence negatively a decision to employ this processing technique for component manufacture but also tend to limit the flexibility in terms of optimizing alloy composition for this particular process. One possibility would be to make use of elemental blends of powders. Not only would the cost of starting materials be significantly reduced but enormous flexibility would be afforded to the process regarding modifying composition either before or indeed during processing. The problem with this approach is that during the very small dwell time that the material is liquid, thorough mixing must occur. The rapid rate of heat extraction exacerbates this problem. However, we have postulated, and demonstrated, that if the combination of elements being mixed has a significant negative heat of mixing, then an additional source of heat is present exactly where required to effect efficient blending.

The original part of this work was impacted by the absence of the LENS™ device. The plan to produce the alloys listed in the proposal is now underway, and the results of these experiments will be presented in the next summary report. However, as part of the studies involving elemental blends and the production of new alloys, the alloy Ti-1B (wt.%) has been produced from elemental blends of Ti and B powders. This composition was chosen to investigate the possibility of producing new alloys using LENS™, in this case a Ti alloy hardened by a dispersion of borides. This composition is ideally suited to processing as elemental blends as the heat of mixing, ΔHmix, is given by ΔHmix$\approx$-22Kcals/gatom, and so significant generation of heat is expected to accompany mixing of these powders in the liquid state. As can be seen in Fig. 5, a refined dispersion of borides has been

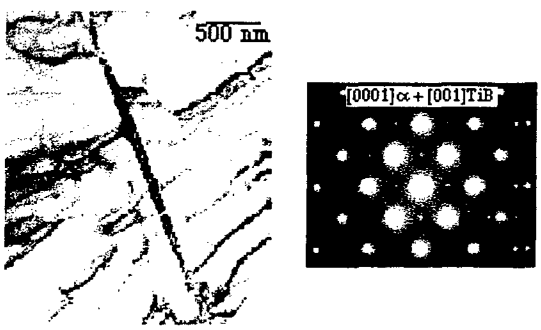


Fig. 6. TEM micrograph and representative diffraction pattern of a lenticular precipitate of TiB in Ti produced in-situ by LENS™.

produced. From the diffraction patterns recorded under a variety of zone axes (one of these shown in Fig. 5), it is possible to identify these particles as TiB, which exhibit an orientation relationship given by:

(11~20)α ll (010)TiB
[1~101]α ll [001]TiB

This is a very exciting result. In addition to these fine particles, there are also long lenticular particles present, see Fig. 6, also identified as TiB, but exhibiting the expected orientation relationship given by:

(11~20)α ll (010)TiB
[0001]α ll [100]TiB

These two types of morphology for TiB particles probably correspond to different formation mechanisms. Thus, the more conventional lenticular particles most probably were formed during cooling from near the melting point, whereas the refined distribution of particles was formed from decomposition of a supersaturated solid solution during subsequent processing (i.e., re-heating during subsequent exposure to the laser beam).

Work performed during the second year focused on extending the research into ultrafine dispersions of TiB as well as an investigation of the effect of the heat of mixing and processing on mechanical properties of industrially relevant alloys. For the investigation of the heat of mixing and processing variables on mechanical properties, β-21S was selected as a candidate alloy.

This alloy was deposited from three different starting powder stock: pre-alloyed Timetal 21S, an elemental blend of Timetal 21S, and an elemental blend of a modified alloy where the Mo was replaced by an equivalent amount of Cr. This modified alloy has a target composition of Ti-9.4Cr-2.7Nb-3Al-0.2Si – wt%, a composition chosen based on the relative ability of an element in stabilizing the β- phase. The factors that are proposed to affect the enthalpy of mixing are given in Table 2. The absorbtivity only plays a role when the powder is in the solid state. Once it has entered the melt pool, the laser absorbtivity no longer plays a role in determining chemical homogeneity.

Table 2: Physical and Thermodynamic properties affecting chemical homogeneity

Variable	Ti	Mo	Cr	Al	Nb	Si
ΔHmix (with Ti) (KJ/mol)[7]	---	-16	-32	-137	+10	-70
ΔHfusion (KJ/mol) [8]	15.447	32.539	16.933	10.795	26.068	50.551
Absorbtivity (%)	45	32.1	36.9	7.8	18.5	---

The ΔHfusion for the Timetal 21S and Cr-modified Timetal 21S is 16.8 KJ and 15.6 KJ, respectively. These numbers are based on a simple rule of mixtures approach for the two different elemental blend mixtures.

Figure 7 shows both the Timetal 21S and the Cr modified Timetal 21S. Each image in figure 7 is a backscattered SEM micrograph where the difference in contrast is elemental in nature. It can be observed that at lower power densities, particularly in the Timetal 21S with Mo, there is a large fraction of unmelted powder. There were no instances of partially unreacted chromium in the chromium modified Timetal 21S. By 7.5 KJ/in^3 for the unmodified Timetal 21S case, and by 4.5

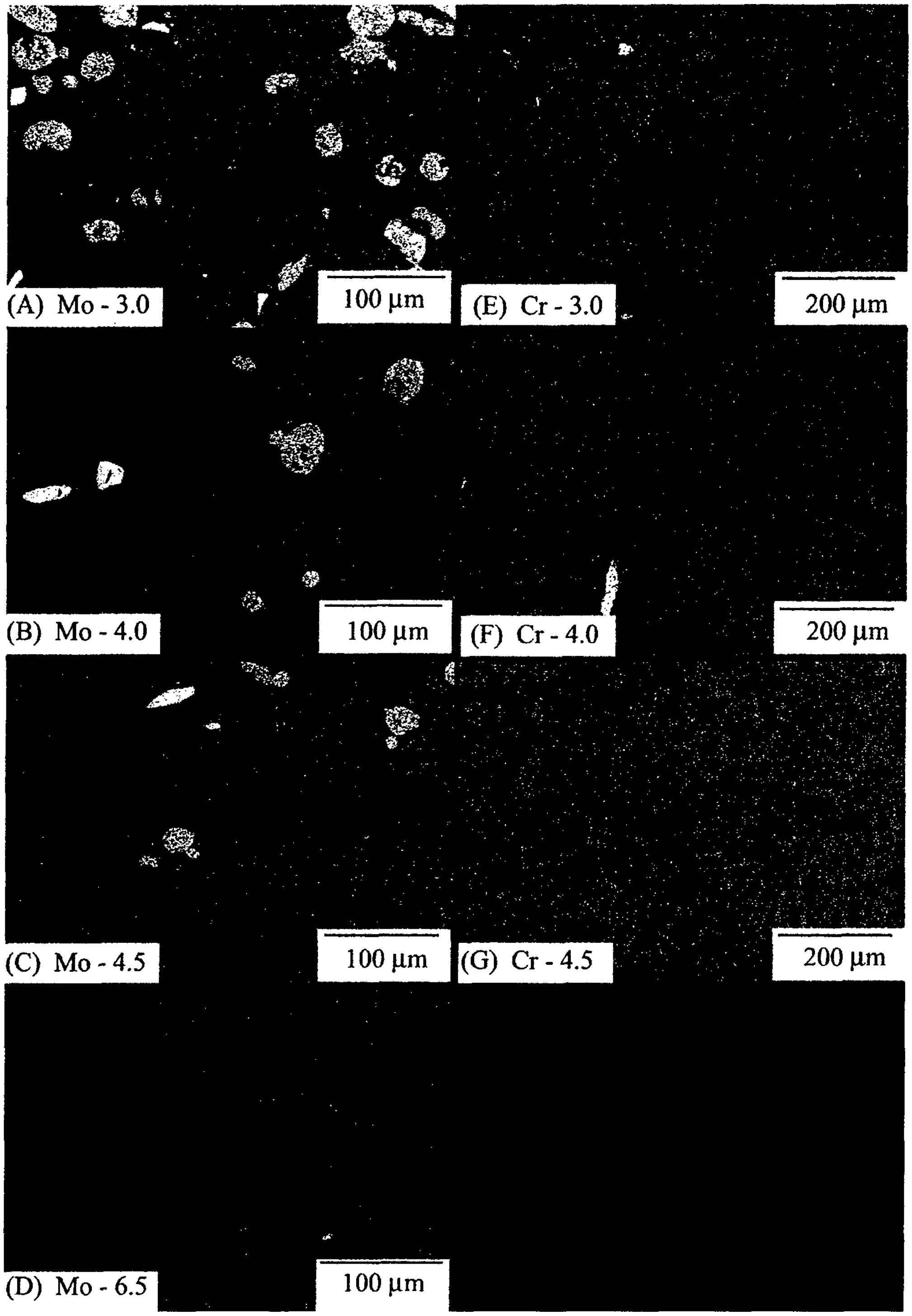


Fig. 7: Comparision of elemental β-21S and Cr-modified elemental β-21S given different energy densities.

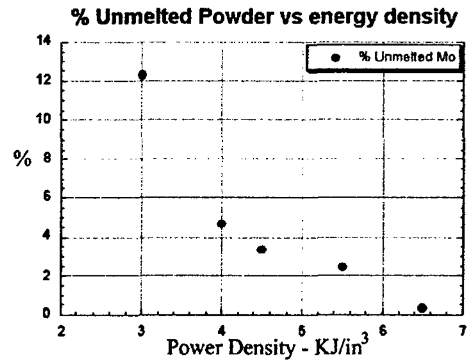


Fig. 8: Fraction unmelted vs. energy density

KJ/in^3 for the chromium modified Timetal 21S case, the scale and morphology of α within the β matrix was nearly identical with the pre-alloyed Timetal 21S case.

Standard quantitative stereological procedures have been used to determine the effect of energy density on the volume fraction of unmelted elemental powder in both cases. In the case of the unmodified Timetal 21S, the fv unmelted Mo starts at roughly 15% at 3.0 KJ/in^3, and drops down to 1% by 6.5 KJ/in^3. Additionally, the fv of unmelted Ti holds at a constant 2%, independent of power density. Figure 8 shows these results. For the case of the chromium modified Timetal 21S, the volume fraction of unmelted titanium and niobium are the only measurable features. These are both at such minimum volume fraction as to be difficult to quantify using the point count method. It was observed that by 4.5 KJ/in^3, all of the elements had reacted. The composition of the alloys was also measured. The deposited Timetal 21S with a target composition of Ti-15Mo-3Al-2.7Nb-0.2Si had an actual composition of Ti-16Mo-5Al-3Nb-0.6Si. The as-deposited Cr-modified Timetal 21S with an ultimate target composition of Ti-9.4Cr-3Al-2.7Nb-0.2Si, and a starting powder composition of Ti-13Cr-2Al-2.7Nb-0.2Si, had an actual composition of Ti-11.4Cr-2.2Al-2.45Nb-0.7Si. These compositions were used to calculate the ΔH_{fusion} of the alloys using a simple rule of mixtures approach. The calculated values were 17.1 KJ for the unmodified alloy, and 16.0 KJ for the Cr-modified alloy. It was observed that the power density did not have an effect on the composition, indicating that none of the elements were preferentially affected during the deposition process. Although each of these alloys is outside what was targeted, they both are close so that starting powder composition could be modified to achieve the desired alloy composition.

The TiB work has lead into other programs such as the development of creep resistant titanium alloys. The heat of mixing and alloy development continue to be of interest to us, as demonstrated by the deposition of RR-BurTi, a non-burning titanium alloy with carbide despersoides.

4. Pre-forms for Forging of Unitized Structures

Motivation: Direct laser deposition offers a significant potential for the production of net-shaped components. However, for a number of high performance applications, typical of components for aerospace, it will be necessary to subject the materials to thermomechanical processing following deposition. In fact, the use of direct laser deposition to produce pre-forms for forging, for example, affords unique possibilities in terms of the exploration of

novel alloy compositions and heat-treatments. For instance, using the example given above, it would be possible to locate an α/β alloy with a relatively high β-transus temperature in a region where damage tolerance was required and then vary the composition such that another α/β alloy with a lower β-transus temperature would be located in a region requiring high strength. Forging, at a temperature of 900°C would cause one part of the component to consist of a colony or basketweave microstructure whereas the other location would have a microstructure consisting of equiaxed α-Ti and transformed β-Ti.

Work did not commence on this until the third year of the program. This decision was based on the fact that other microstructural complexities (e.g., the formation of athermal ω and secondary α). During the third stage of the program, blocks of Ti-xAl-yV ($2<x<6$ and $2<y<8$, wt%) were deposited. The blocks were designed so that, after deposition, each would be 50 mm in length, 33 mm in width, and 27 mm in height. The composition profile was established in the z-direction. This composition profile was designed to have three regions, each 9 mm in height, of uni-composition. Each layer of uni-composition had constant aluminum content, while each block had constant vanadium content. Three blocks were deposited with three different vanadium contents (2%, 5%, and 8%), with each block having three different aluminum contents (2%, 4%, and 7%). Thus, a total of 9 different alloys were established.

After the deposition, each block was upset at temperature in a die specifically designed to maintain the composition profile. The die design is shown in figure 9. The thermo-mechanical processing took place under vacuum at 1050°C, and a strain rate of 10^{-3} s^{-1}. The reduction was ~20%, bringing the dimension of 33 mm to 27 mm. This processing was designed to simulate thermo-mechanical processing within the β phase field. After this operation, the block was sectioned for heat treatment according to figure 10. Electro-discharge machining (EDM) was used to section each block into three equal 9 mm slices, with each slice containing three uni-composition regions. Each block was β-solutionized at 1050° C for 10 minutes and then air-cooled. After this step, the slices were aged at different conditions. The first slice was aged at 525° C for 2 hours and air-cooled. The second slice was aged at 525° C for 2 hours and furnace-cooled. The third slice was aged at 725° C for two hours and air-cooled. In this fashion, different microstructures were produced for each composition.After aging, each slice was cut using EDM so that the uni-compositions were separated. Thus, 27 samples were sent out for mechanical testing. Low-stress grinding was used to prepare tensile specimens 50 mm in length, with a gauge length of 30 mm and a diameter of 4

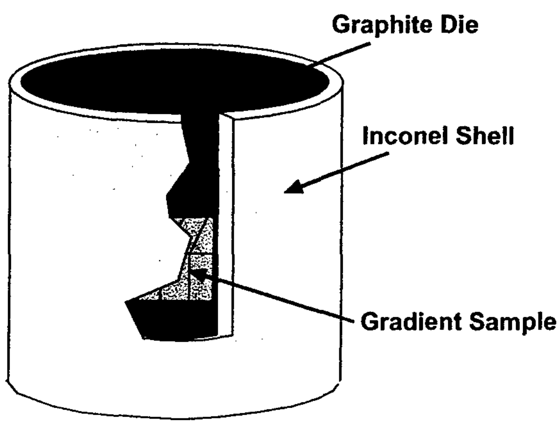


Fig. 9: Cut away of die design for forging preforms and the combinatorial method.

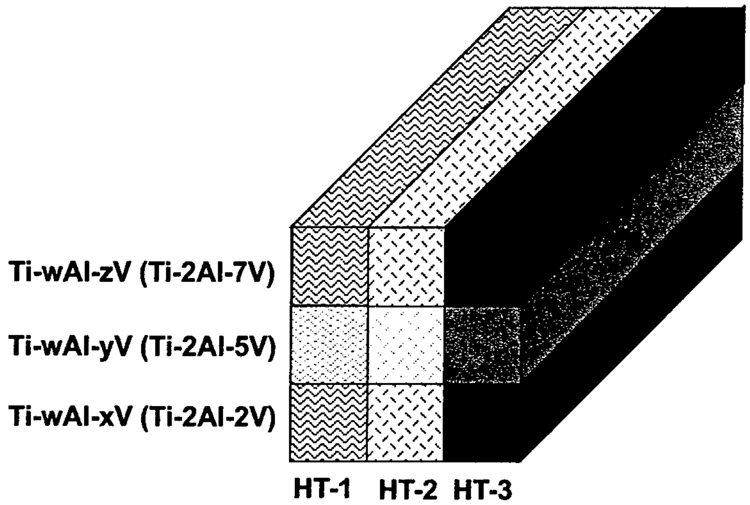


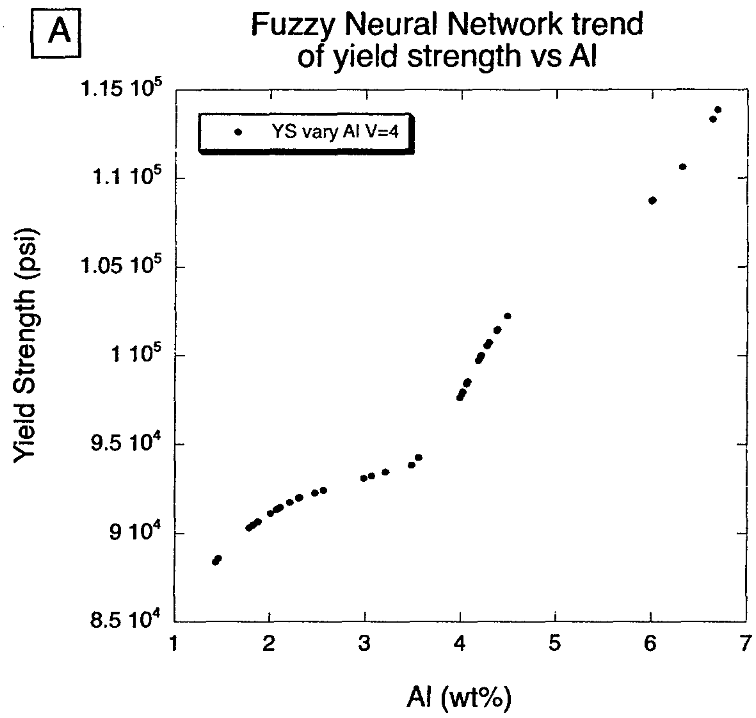
Fig. 10: Schematic of regions of the sample to be machined into tensile bars of varying composition thermal histories.

mm. Each was subjected to room temperature tensile testing.

After testing, the first relationship that was determined was the relationship between the compositional variables and the mechanical properties. The alloying additions in this database are aluminum and vanadium. Additionally, Fe, Cu, O, N, and H were measured. However, the quantity of each of these elements was constant, so they will be neglected. Figure 11a shows the effect of aluminum on the yield strength (YS) and ultimate tensile strength (UTS), while figure 11b shows the effect of vanadium on the yield strength (YS) and ultimate tensile strength (UTS). Notice that the properties increase with both increasing vanadium and increasing aluminum content in the alloys.

Work was also performed relating microstructure and properties, and composition-microstructure. It was observed that the aluminum content is critically important in the formation of a colony microstructure. With either too little aluminum, or too much vanadium, the microstructure tends to always be a basketweave microstructure. In Ti-6Al-4V, both are easily obtained, lending to the idea that this alloy is optimal for large variations in microstructure.

The work performed in this final task show that not only can LENS™ deposited material be used for forging performs, but that the composition control can be maintained throughout the forging operation, and that such material can be further tested in the combinatorial approach.



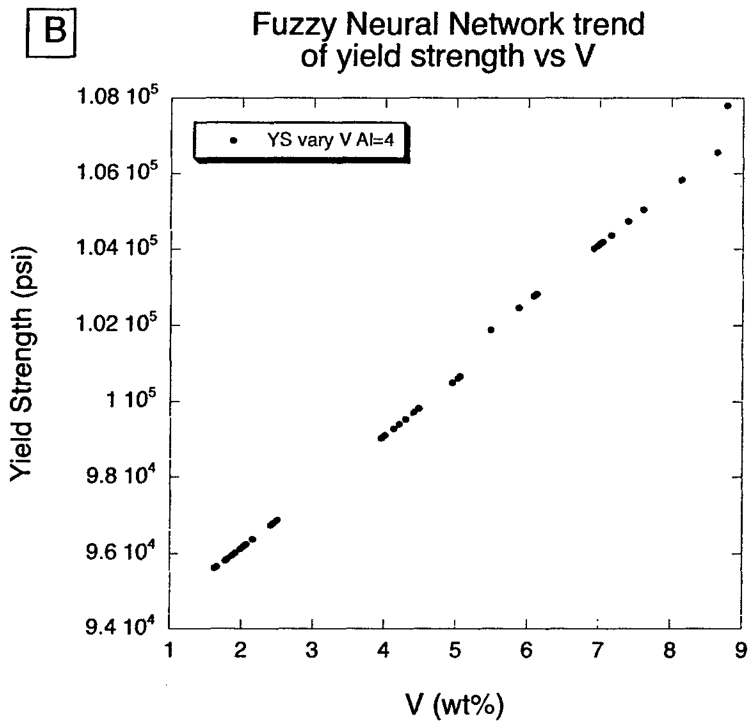


Fig. 11: Fuzzy Logic Models of YS vs. composition

Students Graduated
During the scope of this work, 2 students graduated with masters degrees and 1 with a PhD.

Publications

1. Phase Evolution in Laser Deposited Titanium-Chromium Alloys, 2002, *Metall. and Mater. Trans. A*, 33, 2129. With R. Banerjee and P. C. Collins.

2. Laser Deposition of *In Situ* Ti – TiB Composites, 2002, *Advanced Engineering Materials*, 4(11), 847. With R. Banerjee and P. C. Collins.

3. Microstructural Evolution in Laser Deposited Compositionally Graded α/β Titanium-Vanadium Alloys, 2003, *Acta Mater*, 51(11), 3277. With R. Banerjee, P. C. Collins, D. Bhattacharyya, and S. Banerjee.

4. Direct Laser Deposition of In Situ Ti-6Al-4V - TiB Composites, 2003, *Mater. Sci. Eng. A*. 358, 343. With R. Banerjee, P. C. Collins, and A. Genc.

5. Microstructural Evolution in Laser Deposited Compositionally Graded α/β Titanium-Vanadium Alloys, 2003, *Acta Mater.*, 51(11), 3277. With R. Banerjee, P. C. Collins, D. Bhattacharyya and S. Banerjee

6. Laser Deposition of Compositionally Graded Titanium-Vanadium and Titanium-Molybdenum Alloys, 2003, *Mater. Sci. and Eng. A,* 352(1-2), 118. With P. C. Collins, R. Banerjee, and S. Banerjee,

7. The influence of the enthalpy of mixing during the laser deposition of complex titanium alloys using elemental blends, 2003, *Scripta Mater.*, 48(10), 1445. With P. C. Collins, and R. Banerjee

8. Direct Laser Deposition of *In Situ* Metal Matrix Composites Based on Titanium Borides, 2003, to appear in *Titanium 2003: Proceedings of the Tenth World Conference on Titanium.* With R. Banerjee, P. C. Collins, A. Genc, and J. Tiley

9. Phase Transformations in Compositionally Graded Titanium Alloys, 2003, to appear in *Titanium 2003: Proceedings of the Tenth World Conference on Titanium.* With R. Banerjee, P. C. Collins, D. Bhattacharyya, and S. Banerjee

10. A Combinatorial Approach to the Development of Neural Networks for the Prediction of Composition / Microstructure / Property Relationships in α/β Ti Alloys, 2003, to appear in *Titanium 2003: Proceedings of the Tenth World Conference on Titanium.* With P. C. Collins, S. Connors, and R. Banerjee

11. Precipitation of Grain Boundary Alpha in a Laser Deposited Compositionally Graded Ti-8Al-xV Alloy – an Orientation Microscopy Study, 2004, Acta Mater., 52, 377. With R. Banerjee, D. Bhattacharyya, P. C. Collins, and G. B. Viswanathan.

12. Comparison of Microstructural Evolution in Laser Deposited and Arc-Melted *In Situ* Ti – TiB Composites, 2004, *Metall. Mater. Trans.* A, 35(7), 2143. With R. Banerjee, A. Genc, and P. C. Collins

13. Compositionally graded materials by laser engineered net shaping (LENS™), 2004, to appear in *Intermetallics*. With P. C. Collins, G. B. Viswanathan, and R. Banerjee